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13. ABSTRACT (Maximum 200 words)

Abstract:
The report highlighted the progress by Liu and Grinstaff group on the development of nanoscale structures and sensors. We have made progress along several directions under ARO support, including:
1. Developed an enabling technology to directly deposit metal, semiconductor and conducting polymer nanostructures on surface. The technology, electrochemical dip-pen nanolithography (EDPN), is based on electrochemical reactions within a tiny water meniscus between an Atomic Force Microscope (AFM) tip and surface structures. We have shown that it can be used as a versatile tool to not only create nanostructures of various materials on surfaces, but also to modify existing nanostructures at specific locations to fabricate novel devices.
2. Nanoscale junctions made of different materials can be created by EDPN technique. Nanoscale junctions between polyanniline and polythiophene can be easily created. Such junctions can function as nanoscale electronic devices such as diodes and light emitting diodes.
3. EDPN can be used to modify the surface of nanotubes to change their electronic properties. By selecting the right chemical to deposit onto the nanotubes surfaces, the nanotubes can be changed from p type semiconductors to n-type semiconductors.
4. A new method that can grow single walled carbon nanotubes with precise control of locations and orientations has been developed. This is the first time such high degree of control has been demonstrated for one-dimensional nanomaterials. The capability to control the location and orientation of nanotubes makes the large scale fabrication of nanotube electronics a possibility.
5. An international workshop on the DNA Supramolecular Assemblies was held at Avignon, France on the 5th-6th of May, 2004.

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(1) List of papers submitted or published under ARO sponsorship Since September 18, 2000:

(1)   "Mobile ambipolar domain in carbon-nanotube infrared emitters", Marcus Freitag, Jia Chen, Jerry Tersoff, James C. Tsang, Qiang Fu, **Jie Liu**, and Phaedon Avouris, *Physical Review Letters,* **93**, Art. No. 076803 (2004).

(2)   "Chemical vapor depositions of single-walled carbon nanotubes catalyzed by uniform Fe2O3 nanoclusters synthesized using diblock copolymer micelles", Qiang Fu, Shaoming Huang, **Jie Liu**, *J. Phys. Chem. B,* **108**(20), 6124-6129 (2004).

(3)   "Growth Mechanism of Oriented Long Single Walled Carbon Nanotubes Using "Fast-Heating" Chemical Vapor Deposition Process", Shaoming Huang, Mike Woodson, Richard Smalley and **Jie Liu**, *Nanoletters*, **4**(6), 1025-1028(2004).

(4)   "Polymer electrolyte-gated nanotube field-effect carbon transistor"*,* C.G. Lu, Q. Fu, S.M. Huang and **J. Liu**, *Nano Letters*, **4**(4), 623-627 (2004).

(5)   "Controlled Growth of Long GaN Nanowires from Catalyst Patterns Fabricated by "Dip-Pen" Nanolithographic Techniques", Jianye Li, Chenguang Lu, Benjamin Maynor, Shaoming Huang, and **Jie Liu**, *Chemistry of Materials***, 16**(9), 1633-1636 (2004).

(6)   *"*Growth of aligned SWNT arrays from water-soluble molecular clusters for nanotube device fabrication*",* S.M. Huang, Q. Fu, L. An and **J. Liu**, *Physical Chemistry Chemical Physics*, **6**(6), 1077-1079 (2004).

(7)   *"*Ultralong, well-aligned single-walled carbon nanotube architectures on surfaces*",* S.M. Huang, B. Maynor, X.Y. Cai and J. Liu, *Advanced Materials,* **15**(19), 1651 (2003).

(8)   *"*Growth of millimeter-long and horizontally aligned single-walled carbon nanotubes on flat substrates*",* S.M. Huang, X.Y. Cai and **J. Liu**, *Journal of the American Chemical Society*, **125**(19), 5636-5637 (2003).

(9)   *"*Direct-writing of polymer nanostructures: Poly(thiophene) nanowires on semiconducting and insulating surfaces*",* B.W. Maynor, S.F. Filocamo, M.W. Grinstaff and **J. Liu***, Journal of the American Chemical Society*, **124**(4), 522-523 (2002).

(10)   *"*Tungsten oxide nanowires on tungsten substrates*",* G. Gu, B. Zheng, W.Q. Han, S. Roth and **J. Liu**, *Nano Letters*, **2**(8), 849-851 (2002).

(11)   *"*Au "ink" for AFM "dip-pen" nanolithography*",* B.W. Maynor, Y. Li and **J. Liu**, *Langmuir*, **17**(9), 2575-2578 (2001).

(2) Scientific personnel supported by this project:

Mr. Benjamin Maynor, graduate student graduates in May 2004. His stipend was paid through Gates Millennium Fellowship but he is working on this project full time.

Mr. Shaun Filocamo, graduate student.

Dr. Shaoming Huang (50% effort). Senior research associate working on the growth and chemical modification of nanotubes

(3) Report of Inventions

N/A

(4) Scientific progress and accomplishments

1. Electrochemical DPN of Polymeric nanostrutcures

Over the last year we have further developed an enabling technology to directly deposit metal, semiconductor and conducting polymer nanostructures on surface. The technology, electrochemical dip-pen nanolithography (EDPN), is based on electrochemical reactions within a tiny water meniscus between an Atomic Force Microscope (AFM) tip and surface structures. We have shown that it can be used as a versatile tool to not only create nanostructures of various materials on surfaces, but also to modify existing nanostructures at specific locations to fabricate novel devices.

Electrochemical Dip-Pen Nanolithography is a new and recently reported AFM lithography technique. E-DPN, like other DPN techniques, relies on spontaneous condensation to facilitate transport of material from the AFM tip to the surface. A chemical process, such as covalent bonding or an electrochemical reaction, then immobilizes the deposited material on the surface. Since the reaction occurs at the AFM tip, material deposition localizes on the patterns traced by the tip. As the name of this technique implies, patterning of nanostructures is like "drawing with a pen." Using DPN techniques, nanostructures composed of organic, semiconducting, or metallic materials are easily obtained of controlled and well-defined nanometer shape and size. In this report, we electrochemically polymerized 3,4-ethylenedioxythiophene (EDOT) and polyaniline and created nanostructures with nanoscale junctions between different materials. More importantly, we have shown that EDPN is an excellent method for the local chemical modification of nanostructures.

2. Creation of Nanoscale junctions Using EDPN:

Nanoscale junctions between two different polymeric materials can be created by EDPN technique. Nanoscale junctions between polyanniline and polythiophene can be easily created. Such junctions can function as nanoscale electronic devices such as diodes and light emitting diodes.

Figure 1a shows a line of polyaniline formed on the Si wafer using this method. The line is 1 μm in length and 1.61 nm in height. Figure 1b shows a line of polypyrrole with dimensions of 1 μm in length and 1.64 nm in height. In these experiments, polymer lines formed from aniline, EDOT, or pyrrole typically were drawn with dimensions of 1 μm in length, 1.5-3 nm in height, and 100-150 nm in width.

The applied voltage to form the polymeric nanostructure depends on the thickness of the native oxide layer and the type of monomer on the tip. Typical bias voltages

ranged from –7 to –10 V. At such high negative voltages, surface oxidation can compete with the electrochemical polymerization. To insure polymer was being deposited, we used an uncoated AFM tip under identical conditions to prepare a 2 μm SiO_2 line. These lines were then subjected to a 1:2 solution of H_2O_2:H_2SO_4, a strongly oxidizing solution that will quickly degrade the polymer compared to the SiO_2 line. After 5 minutes, the SiO_2 (left-hand line; Figure 2) had decreased in height on average 55%, while the polyaniline (right-hand line; Figure 2) had decreased in height on average 90%, consistent with the difference in the chemical composition of the lines. Along with oxidation of the polymer lines, this solution oxidizes the background Si, decreasing the observed height of the drawn SiO_2 structures.

Similar results were observed with the polypyrrole lines, as shown in Figure 3. After 15 minutes, both lines had been affected, but again at different degradation rates. The SiO_2 (left-hand lines; Figure 3) had decreased on average 60%, while the polypyrrole (right-hand lines; Figure 3) had decreased on average 95%, again consistent with differing chemical composition of the two types of lines. The residual height is likely a consequence of silicon oxidation during the polymerization process.

The polyaniline line shown in Figure 2 was drawn at a much faster rate (0.095 μm/sec) than polypyrrole (0.01 μm/sec), and is more susceptible to the deposition conditions. Polyaniline drew easier at humidity levels closer to 40%, while the polypyrrole lines were drawn at 49%. One explanation for the humidity dependence is the difference in water solubility between aniline (1 g in 28.6 mL water) and pyrrole (negligible). The humidity of the air affects the size of the water meniscus that forms between the tip and the surface. As soon as the water meniscus is formed, capillary action would siphon off aniline, leaving less "ink" on the tip for subsequent polymerization. The applied voltage also plays a significant role in the deposition process of these features, since no polymer lines are deposited without an applied voltage. Two mechanisms are currently under investigation. The first mechanism involves the deposition of large oligomers formed in the water meniscus as the tip translates across the surface. Alternatively, charged species collect at the surface and subsequent polymerization affords the polymeric nanostructures. Changes to the interfacial properties of both the tip and the surface are being investigated to characterize and understand the transport and deposition mechanism from the tip.

One important advantage of this technique is that nanoscale junctions composed of the same or different materials can be easily fabricated. Figure 4 shows an interconnect made from two polypyrrole lines, while Figure 5 shows an interconnect made from lines of two different compositions: polyaniline and poly(ethylenedioxythiophene) (PEDOT). The homopolymer interconnect was formed from the same tip within a minute, using slightly different lithography conditions to ensure adequate "ink" for drawing of the second line. The interconnect formed from different polymers was prepared in two steps since the tip needed to be exchanged for each polymer. To confirm the identity of the two lines, we scanned the lines with a Au-plated tip, since Au has a higher affinity for sulfur over nitrogen. A tapping-mode tip was coated first with 4 nm of Ti and then 20 nm of Au. As this Au-plated tip was scanned over the lines at a 45° angle to the nanostructure, the phase change picture displayed a more pronounced line for PEDOT compared to polyaniline. This result

shows the lines are chemically different, since the Au-plated tip interacts preferentially with PEDOT.

3. Growth of aligned single walled carbon nanotubes:

A new method that can grow single walled carbon nanotubes with precise control of locations and orientations has been developed. This is the first time such high degree of control has been demonstrated for one-dimensional nanomaterials. The capability to control the location and orientation of nanotubes makes the large scale fabrication of nanotube electronics a possibility.

The growth of SWNTs was carried out by CO-CVD in a two-furnace setup. The feeding gas was CO/H_2 mixture and the catalysts were monodispersed Fe/Mo nanoparticles dispersed or patterned photolithographically on SiO_2/Si wafers. All samples described in this report were grown at 900 °C for 10 minutes. Normally only short and randomly oriented SWNTs were observed on substrate surfaces (Figure 6a). These nanotubes are normally less than 5 micrometers with occasionally long SWNTs of several tens micrometers and has been shown to be SWNTs. However, when the substrate with the catalysts was heated using a quick heating process in CO/H_2 flow to the desired reaction temperature (900°C), ultra-long, well-aligned SWNTs arrays were produced. Figure 6b is the typical SEM image of the as-grown SWNT arrays on the surface. Under this magnification, individual nanotubes were shown as bright lines under SEM. Comparing with nanotubes in Figure 6, they have very similar characteristics. In addition, AFM measurements have shown that the heights of the nanotubes were between 1-2.5 nm, in good agreement with previous results of SWNT growth under similar growth conditions. Most of the as-grown SWNTs are relatively straight and have the lengths of several hundreds micrometers after 10 minutes growth. The longest one we have observed is longer then 2 mm which is the longest individual SWNT ever reported (Figure 7). The growth rate is estimated to be more than 200 µ/minute. Such nanotubes make the evaporation of multiple metal electrodes on a single nanotube a relatively easy task. Thus, multiple devices can be created on the same nanotubes along its lengths. This added processibility is desirable for large scale device fabrications.

More importantly, such a capability also enables us to growth more complicated two dimensional nanotube frameworks on substrates that can not be produced otherwise. Although SWNTs are considered as an ideal system for molecular electronics and individual SWNT has been demonstrated as devices such as field-effect transistor, assembling SWNTs into multi-terminal devices and complex circuits remains great challenge. Our successful growth of long isolated nanotubes on surface with controllable direction and location makes it possible to fabricate such multi-dimensional and multi-layer crossed-networks. As shown in Figure 8, we have fabricated well-defined crossed-network structures of SWNTs in large scale by a two-step growth process. These images showed that we could easily fabricate crossed nanotubes by orienting the Si wafers along different directions during the two growth steps. Basically, two-dimensional crossed-networks with any angle can be easily fabricated using such a process.

In summary, we have developed a simple method to produce millimeter-long, isolated and well-orientated SWNT arrays in large scale on flat surface without the use of any external force like electric and magnetic fields. The length of the nanotubes can be a few millimeters and their orientations can be easily controlled by changing the orientations of the substrates with respect to the gas flow directions. Two dimensional

crossed-networks of nanotubes can be easily fabricated using a two-step process. In addition, the lengths of the nanotubes can be controlled by either patterning the catalysts with desired separations or simple cutting with a blade. These results have shown that we have gained much more controls, including the control of orientations, locations and lengths, in the synthesis of SWNTs. They represent a breakthrough in the controlled production of aligned SWNT arrays in large scale and a big step forward toward the SWNT-based nanotechnology.

(5) Technology transfer:

N/A

(6) Other:

1. A symposium focusing on nanoscale chemical and biological sensors has been organized at the American Chemical Society Annual Meeting. The symposium brings together top scientists working in the field for an one-day meeting on March 24th in New Orleans.

2. We have provided single walled nanotube samples to Professor John Yates's group at University of Pittsburgh to support his on-going ARO supported research programs. After certain chemical treatment and characterization, come of the samples will be sent to researchers at The Edgewood Chemical and Biological Center, US Army.

3. An international Workshop on DNA Supramolecular Assemblies washeld at Avignon, France on the 5th-6th of May, 2004. The fund from ARO was used to pay for the airline tickets and hotel expenses for invited speakers and fees for using the facilities at the University of Avignon.

Figures:
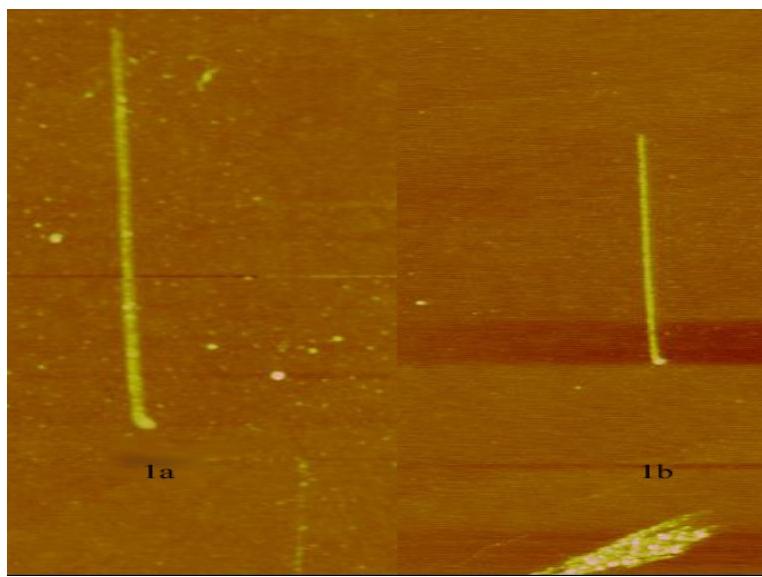
**Figure 1**. AFM images of a polyaniline line (1a) and a polypyrrole line (1b) drawn using E-DPN.

Ave Height 1a: 1.764 nm
Ave Height 2a: 1.607 nm

Ave Height 1b: 0.803 nm
Ave Height 2b: 0.183 nm
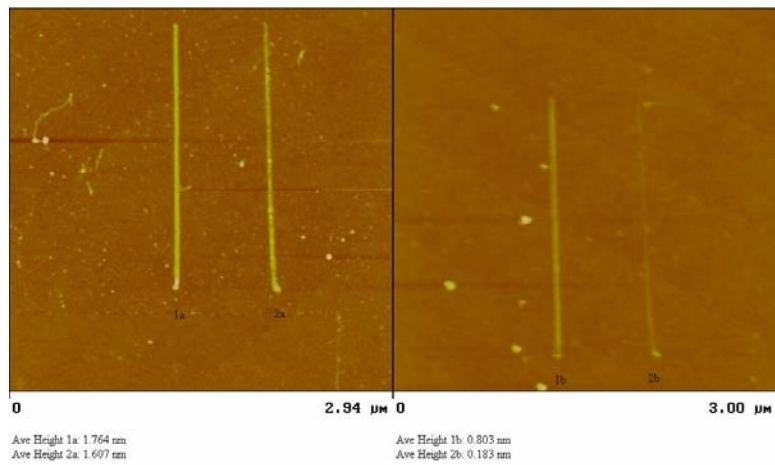
Figure 2. AFM images of SiO$_2$ and polyaniline before (a) and after (b) etching by 1:2 solution of H$_2$O$_2$:H$_2$SO$_4$.

Ave Height 1a: 0.778 nm
Ave Height 2a: 1.207 nm
Ave Height 3a: 1.638 nm
Ave Height 4a: 3.228 nm

Ave Height 1b: 0.311 nm
Ave Height 2b: 0.403 nm
Ave Height 3b: negligible
Ave Height 4b: negligible
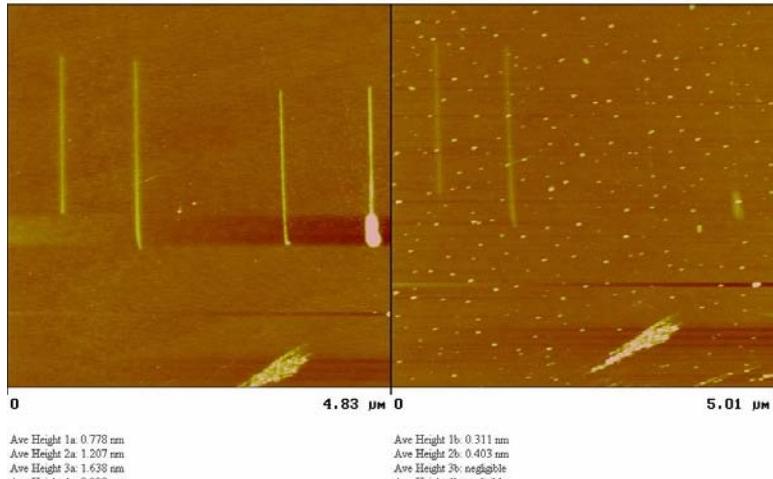
Figure 3. AFM images of two SiO_2 and polypyrrole lines before (a) and after (b) etching by 1:2 solution of H_2O_2:H_2SO_4.
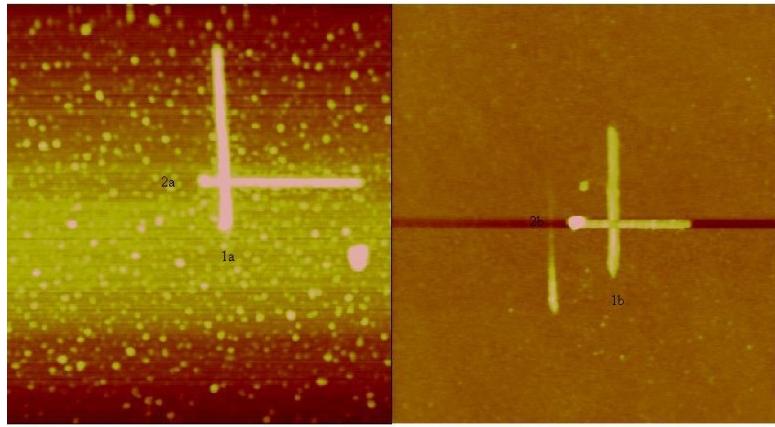
Polypyrrole-polypyrrole cross
Ave Height polypyrrole (1a): 3.4 nm
Ave Height polypyrrole (2a): 4.5 nm
Height of the Intersect: 5.7 nm

Polyaniline-polypyrrole cross
Ave Height polyaniline (1b):   3.219 nm
Ave Height polypyrrole (2b): 2.810 nm
Height of the Intersect: 2.371 nm

Figure 4. AFM image of an interconnect prepared exclusively with polypyrrole, and one constructed from polyaniline and polypyrrole.

Ave Height of polyaniline (A):   1.615 nm
Ave Height of PEDOT (B):   1.971 nm
Height of the Intersect: 2.264 nm
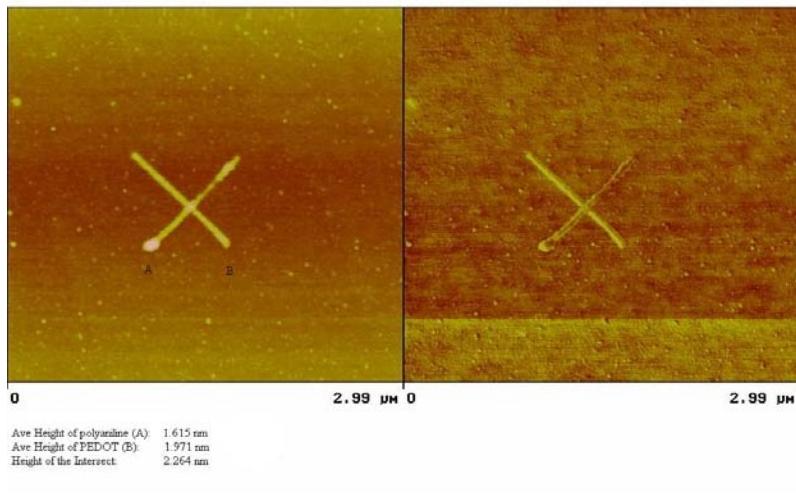
Figure 5. AFM image of an interconnect formed with polyaniline and PEDOT, and the phase change image of this nanostructure.
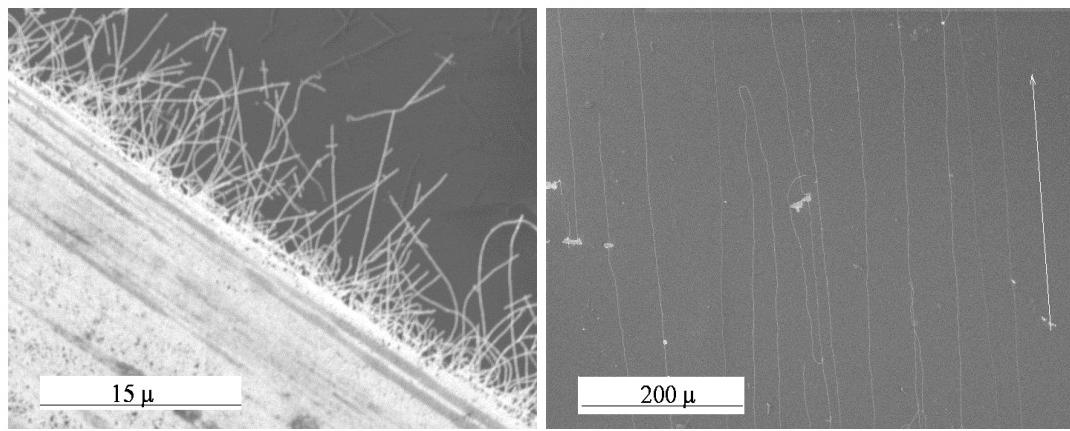
**Figure 6**. SEM image of SWNTs prepared using a) Normal heating and b) Fast heating process.
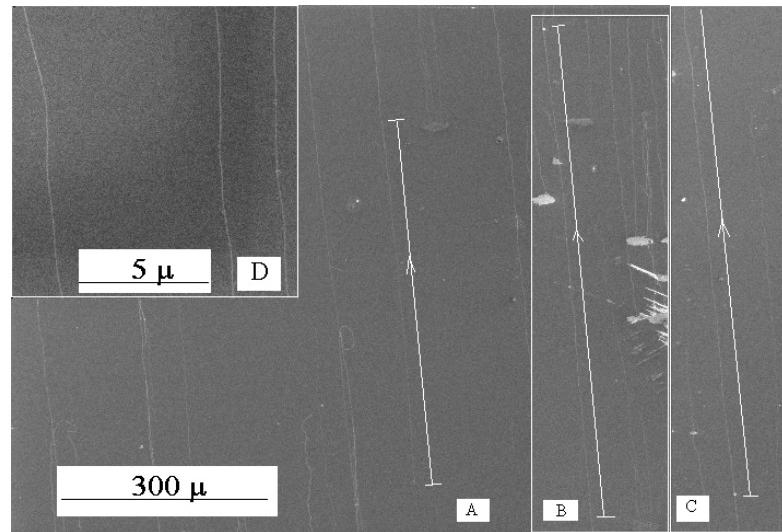
Figure 7. One long nanotubes shown in three SEM images. The white arrows in section A, B and C highlight the starting and connecting points of the same nanotube. Section D shows a high magnification SEM image of the aligned nanotubes.
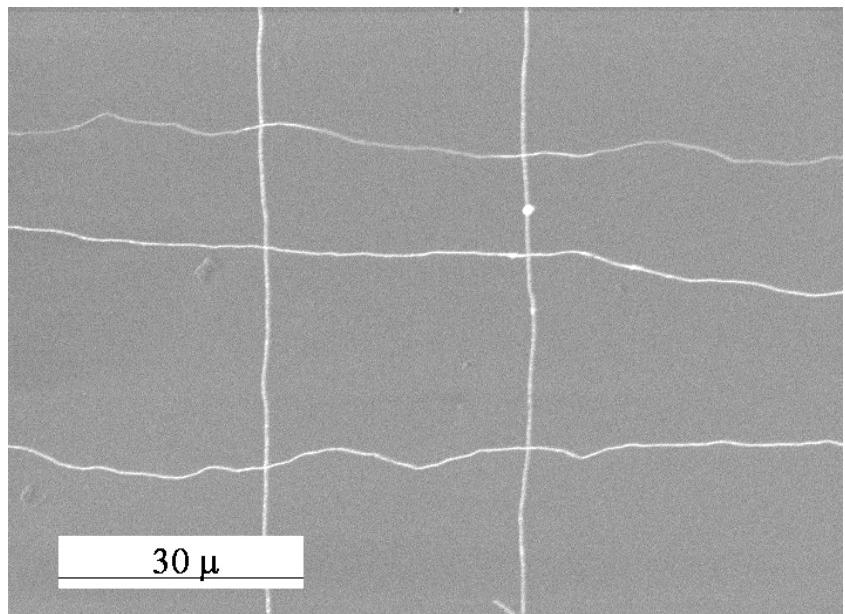
Figure 8. SEM image of two dimensional nanotube network.